

Dissolved organic phosphorus in the Mississippi River plume during spring and fall 2002

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Abstract

Dissolved organic phosphorus (DOP) may play an important role in controlling primary productivity in coastal systems. In an attempt to understand the controls on seasonal and spatial variability in the Mississippi River plume, DOP samples were collected during spring and fall 2002. DOP concentrations were determined using an autoanalyzer with in-line thermal/UV oxidation. For both seasons, DOP concentrations were highest in the river and decreased with distance from the river. Salinity, chlorophyll *a*, dissolved organic carbon and nitrogen are parameters which have been shown to correlate with DOP in other systems. Within the Mississippi River plume, no correlation was found between DOP and any of these parameters, and less than 5% of the total dissolved phosphorus was high molecular weight, as separated by tangential flow ultrafiltration. Our results suggest that DOP may cycle quickly in the plume and be a source of inorganic phosphorus in the late summer, leading to seasonal changes in the inorganic N/P ratio and potentially a shift in the planktonic community.

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1. Introduction

Phosphorus is an essential nutrient for primary production and can be limiting in marine systems (Benson et al., 1996; Karl and Bjorkman, 2001). In natural waters, it exists in several chemical forms that may be categorized as either inorganic (protonated forms of the PO_4^{3-}) or organic (incorporated into organic molecules) (Thomson-Bulldis and Karl, 1998). These organic forms are of biological origin and include nucleic acids, polyphosphates, phosphorus esters and phosphonates (Clark et al., 1998; Benitez-Nelson, 2000; Kolowith et al., 2001). While it has always

been generally accepted that all plankton can utilize inorganic phosphorus, only in the last 15 years have oceanographers demonstrated that dissolved organic phosphorus (DOP) is available to both phytoplankton and bacteria for production (Ormaza-Gonzalez and Statham, 1996; Huang and Hong, 1999; Monaghan and Ruttenberg, 1999; Mortazavi et al., 2000; Kolowith et al., 2001). In the oligotrophic open ocean, where DOP concentrations may exceed dissolved inorganic phosphorus (DIP) concentrations, phytoplankton utilization of phosphorus from DOP compounds may increase primary production affecting carbon dioxide uptake and eventually carbon burial (Van Cappellen and Ingall, 1996; Thomson-Bulldis and Karl, 1998; Benitez-Nelson and Buesseler, 1999; Kolowith et al., 2001). Because oceanic primary productivity is tightly coupled to atmospheric carbon dioxide levels, phosphorus avail-

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ability is theorized to play an important role in climate cycles on a geologic time scale (Van Cappellen and Ingall, 1996; Kolowith et al., 2001). Within the global oceanic carbon cycle, a disproportionately large amount of fixed carbon is being buried in coastal waters (Bernier, 1982; Hedges and Keil, 1995) and while much of this carbon may be of terrigenous origin, a large amount is autochthonous (Trefry et al., 1994; Hedges and Keil, 1995). Therefore, it is important to quantify organic phosphorus as it is potentially available for primary production in coastal systems and will give us a better understanding of the carbon cycle.

In both the Eel River, California, and Apalachicola Bay, Florida, DOP was found to be a large fraction of the total dissolved phosphorus pool and it contributed to phytoplankton and bacterial production (Monaghan and Ruttenberg, 1999; Mortazavi et al., 2000). Mortazavi et al. (2000) calculated a phosphorus budget for Apalachicola Bay, and found that the phosphorus input to the system was lowest in the summer and the fall, while the maximum input was during a flood event. On the Eel River Shelf, the highest concentration of DOP occurred during the high productivity of the summer months, surpassing the concentration of DIP (Monaghan and Ruttenberg, 1999). Alkaline phosphatase was detected at sites with low concentrations of DIP, which could imply DOP was being utilized as a source of P. In the Atchafalaya River plume, Louisiana, the concentration of DOP at 0 salinity was $<0.1 \mu\text{M}$ and was a maximum (approximately $0.35 \mu\text{M}$) at salinity 8 (Pakulski et al., 2000). Within the main branch of the Mississippi River, organic phosphorus concentrations are somewhat lower (average $0.5\text{--}0.6 \mu\text{M}$) than reactive P concentrations but still potentially account for a large source of P to the adjacent shelf with the largest flux occurring in the spring (Sutula et al., 2004).

Because phosphorus is integrated into the food web, particularly in large molecules such as ATP and DNA, it is predicted that a significant fraction of the DOP may be found in the colloidal size fraction which is abundant in seawater (Koike et al., 1990; Guo et al., 1994). This colloidal fraction comprises a significant portion of dissolved organic matter (DOM) in both seawater (Moran and Moore, 1989; Benner et al., 1992; Guo et al., 1994) and coastal waters (Guo and Santschi, 1997). In addition to molecules of biological origin, phosphorus has been found to adsorb onto iron-oxyhydroxides (Suzumura et al., 1998; Lienemann et al., 1999; Lehtoranta and Pitkanen, 2003) which are predominantly colloidal in estuarine waters (Powell et al., 1996). Low molecular weight phosphorus organic compounds were found to be in higher concentrations than high molecular weight organ-

ic phosphorus compounds in some surface coastal and ocean waters (Ridal and Moore, 1990; Suzumura et al., 1998; Benitez-Nelson, 2000). Previous studies have also found that both high and low molecular weight DOP can be assimilated by bacteria and some phytoplankton (Ridal and Moore, 1990; Cotner and Wetzel, 1992; McKelvie et al., 1993; Suzumura et al., 1998). Therefore, size distribution is not a good indication of biological availability, but determination of size distribution may allow for some conclusions on PO_4^{3-} reactivity.

Dissolved organic phosphorus concentrations and cycling in the Mississippi River plume are poorly understood. Since DOP potentially contributes to the bio-available phosphorus in the system and phosphorus may be a limiting nutrient (Ammerman, 1992; Pakulski et al., 2000), it is important to quantify DOP and to understand the processes controlling the concentration. Therefore, our objectives are to quantify the concentration of DOP in the Mississippi River plume and to correlate these concentrations to other basic parameters such as chlorophyll, DOC and suspended solids. We also conducted ultrafiltration in order to separate the larger (presumably more labile) compounds from the smaller refractory material. This paper presents the results of these measurements and attempts to identify the important processes controlling DOP concentrations in this region.

2. Materials and methods

Samples were collected in the Mississippi River plume (MRP) on two cruises aboard the *R/V Pelican* in March and October of 2002 (Fig. 1). The Mississippi River is the world's seventh largest river and discharges

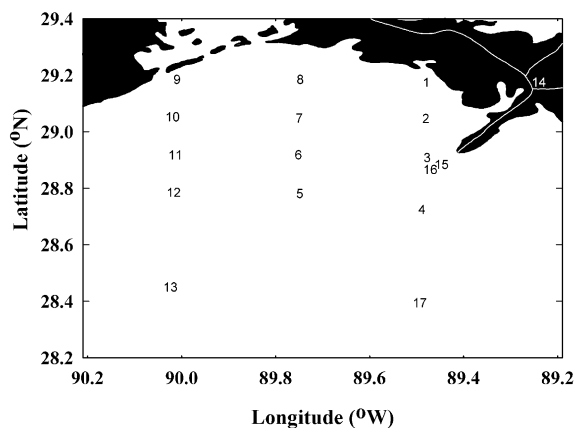


Fig. 1. Station locations for March and October cruises. Each station was sampled between one and four times. Stations 15, 16 and 17 were only sampled in October.

dissolved and particulate material into the Gulf of Mexico enhancing primary production (Lohrenz et al., 1999). The freshwater flow creates a salt wedge estuary form where it discharges into the Gulf of Mexico at Southwest Pass, LA, however it is unconfined by land. The buoyant river plume, which is above the salt wedge, forms when lower salinity waters flow above seawater (Schroeder and Wiseman, 1999). The Mississippi River delivers large amounts of inorganic nitrogen and phosphorus from natural and anthropogenic sources in its drainage basin (Turner and Rabalais, 1991). The cruises were scheduled for March and October to encompass two seasonal flow regimes (spring high flow and fall low flow) however, during the March 2002 cruise, the water discharge was abnormally low at the beginning of the cruise ($14880 \text{ m}^3 \text{ s}^{-1}$ vs. the 30-year average of $22399 \text{ m}^3 \text{ s}^{-1}$) but was increasing dramatically to slightly below the average high flow by the end of the cruise (Fig. 2). These flows would imply that water exiting the mouth of the river would transit the entire study area in less than 2 days (Hitchcock et al., 1997). In October the flow, was abnormally high compared to the 30-year average ($9549 \text{ m}^3 \text{ s}^{-1}$ vs. $8435 \text{ m}^3 \text{ s}^{-1}$), although it was much more consistent throughout the cruise.

Sample sites were chosen on the shelf to represent all areas of the plume with consideration given to covering a wide range of parameters such as salinity, nutrients, chlorophyll *a*, suspended matter and DOC. Samples were also collected at one site within the river (Station 14) and one site in higher salinity waters beyond the main plume (Station 13). In October three stations were added, two that were near the river mouth (Stations 15 and 16) and another in higher salinity waters (Station 17). Stations were occupied between

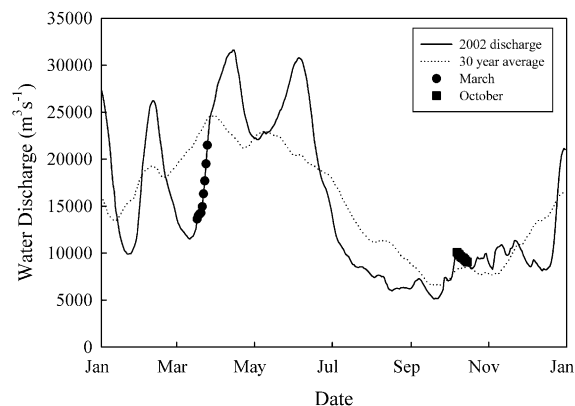


Fig. 2. Mississippi River water discharge from Talbert Landing. The solid line represents 2002 water discharge, dotted line represents 30 year average and circle (●) and square (■) were March and October sampling dates, respectively.

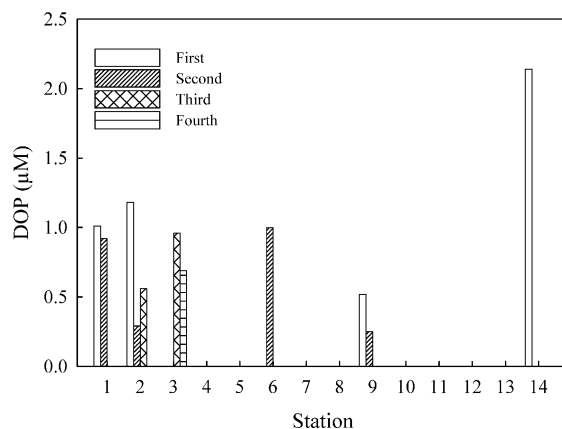


Fig. 3. March surface water DOP concentrations at each station. The bars represent the first, second, third or fourth station occupation within the 10-day sampling period.

one and four times during each cruise in order to assess variability at each station over a short (2–4 days) time frame (labeled as first, second, third and forth in Figs. 3 and 4). At each station, water was collected at 3–4 depths with Niskin bottles attached to a rosette sampler. The depths were chosen to represent surface (1 m) and bottom (2–3 m above the sediment) waters as well as at least one sample immediately below the surface mixed layer. Water was filtered through a $0.2\text{-}\mu\text{m}$ pre-cleaned polysulphone filter and the filtrate was collected in pre-cleaned polyethylene bottles and immediately frozen for later analysis in the laboratory.

Surface water was also collected for ultrafiltration using trace metal clean techniques (Powell and Wilson-Finelli, 2003). Samples were pre-filtered through a $0.2\text{-}\mu\text{m}$ cartridge filter and then 1–2 L were ultrafiltered using a 1-kDa tangential flow ultrafiltration cartridge filter (Gelman Science). The permeate and retentate

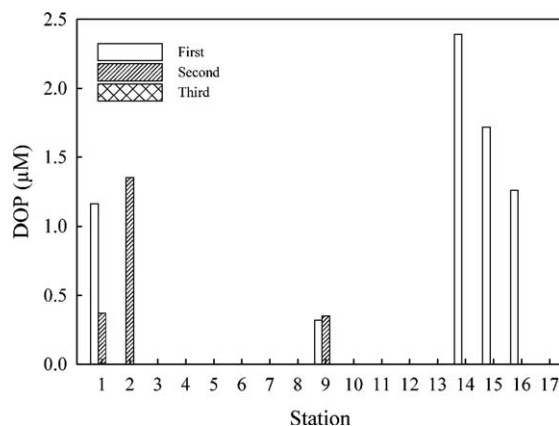


Fig. 4. October surface water DOP concentrations at each station. The bars represent the first, second or third station occupation within the 10-day sampling period.

were collected and frozen for later analysis in the laboratory. We define the colloidal fraction as the calculated concentration of what is retained by the 1-kDa filter but passes through the 0.2- μm pre-filter (Powell et al., 1996). As in Guo and Santschi (1997), the filter was cleaned and calibrated using known molecular weight standards to test the integrity of the filters. These laboratory results indicate a pore size somewhat greater than 1 kDa. Despite the fact that the pore size was larger than 1 kDa, it was used in a manner consistent with current best use practices (Buesseler et al., 1996) and the results allow us to comment on the changing nature (size and conformation) of organic phosphorus in the plume.

Total dissolved phosphorus (TDP) and soluble reactive phosphorus (SRP) were analyzed using a Lachat autoanalyzer flow-injection system with in-line thermal/UV digestion. SRP was analyzed using the molybdenum-blue method of Murphy and Riley (1962). The sample was mixed with a reagent containing ammonium molybdate, potassium tartrate and sulphuric acid, then ascorbic acid was added and a blue complex formed, which is measured using a flow through detector. For the determination of TDP, organic P was first oxidized to SRP with the addition of an alkaline potassium persulfate reagent coupled with heating and UV oxidation. Polyphosphates were oxidized to SRP by sulfuric acid digestion. The sample was then analyzed in a similar manner to SRP. DOP is calculated by subtracting SRP from TDP. Analysis of model compounds for organic phosphate in freshwater and seawater yields recovery efficiencies exceeding 85% for adenosine 5'-triphosphate, 2-aminoethylphosphonic acid and vitamin B-12. We define our limit of detection as 3 times the standard deviation of replicate blank analyses (0.07 μM and 0.6 μM for SRP and DOP, respectively). The higher detection limit for TDP is due to the digestion process which yields a much more variable blank and is associated with the additional reagents. These detection limits account not only for instrumental noise but also for variability in the chemistry of the system. They are much higher than if one defined the detection limit as $3 \times$ signal to noise ratio. Therefore, a sample with a concentration lower than the detection limit might yield an instrumental response but be lower than the detection limit. For all samples with concentrations less than the detection limit, we used 1/2 the detection limit (0.3 μM) in calculating elemental ratios or when comparing to other parameters.

Total dissolved nitrogen (TDN) and nitrate plus nitrite ($\text{NO}_3^- + \text{NO}_2^-$) were sampled using the same procedure as TDP and DIP and analyzed on the same

autoanalyzer. Due to the rapid utilization of ammonium in the MRP (Gardner et al., 1997), we did not determine ammonium. $\text{NO}_3^- + \text{NO}_2^-$ was reduced to NO_2^- in a cadmium column, after which an acidic sulfanilamide colorimetric reagent is added and measured in a flow through detector (Johnson and Petty, 1983). TDN was oxidized to NO_3^- with an alkaline potassium persulfate and analyzed in a similar manner to $\text{NO}_3^- + \text{NO}_2^-$. The detection limit (3 times the standard deviation) for $\text{NO}_3^- + \text{NO}_2^-$ and TDN was 0.07 μM and 0.6 μM , respectively.

Dissolved organic carbon (DOC) samples were analyzed at Tulane University on a Shimadzu 5000 TOC analyzer by high temperature catalytic oxidation (Guo et al., 1994; Wysocki et al., in press). Chlorophyll *a* samples were filtered through a Whatman GF/F filter and extracted with 90% acetone for 12 h, then analyzed by fluorometry (Strickland and Parsons, 1972) using a Turner designs digital fluorometer. Total suspended matter weights were determined by gentle vacuum filtration onto a pre-weighed 47 mm 0.2- μm polycarbonate filters. The filters were rinsed 3 times to remove salt contamination and dried (50 °C) to a constant weight. Salinity and temperature data were collected with a Seabird 911 CTD that was attached to the frame of the rosette sampler.

3. Results and discussion

3.1. Temporal and spatial distributions

The dominant source of phosphorus to many coastal areas is riverine input (Delaney, 1998; Suzumura et al., 1998; Baturin, 2003), and higher concentrations of DOP have been measured during higher discharge (Mortazavi et al., 2000) implying a weathering or flushing effect from the drainage basin. In the Mississippi River plume during 2002, surface water DOP concentrations were highest near the mouth of the river and decreased with distance away from the river during both sampling periods (Figs. 3 and 4). Despite the fact that river discharges during the sampling periods were 16222 $\text{m}^3 \text{s}^{-1}$ in March and 9549 $\text{m}^3 \text{s}^{-1}$ in October the average DOP concentrations in the river were not vastly different in March and October ($2.1 \pm 0.1 \mu\text{M}$ and $2.4 \pm 0.2 \mu\text{M}$, respectively). The spring river flow was lower than the 30 year average of 22399 $\text{m}^3 \text{s}^{-1}$ and the fall flow was higher than the average of 8435 $\text{m}^3 \text{s}^{-1}$. This small difference in the flows may account for a lack of change in the average DOP concentrations in the river and at Station 3 near the river mouth as processes such as river bed scouring

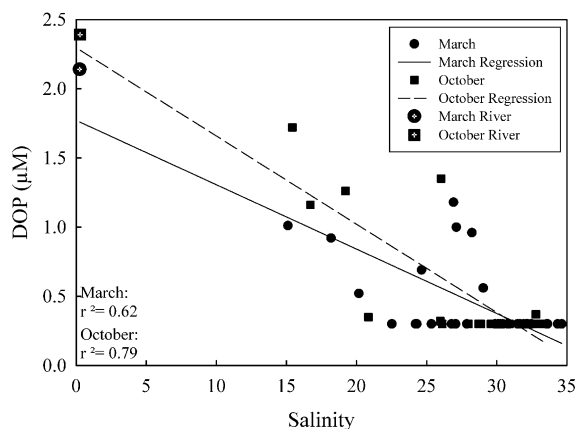


Fig. 5. DOP concentrations as a function of salinity in March (●) and October (■). The symbols with a cross in the center represent the river station.

that would normally occur at higher flows do not occur at these flow rates thus the release of DOP stored in the sediments is limited (Sutula et al., 2004). DOP concentrations were also high at Stations 1 and 9 for both cruises. Station 1 is located close to the coast where there is considerable connection to the river through a somewhat porous levee system. Station 9 is a unique station near Barataria Bay that is quite shallow and other researchers have observed higher concentrations of chlorophyll *a*, DOC, and suspended sediments. During both sampling periods, there was considerable variability in the DOP concentration at all stations indicating processes occurring on time frames shorter than 2–3 days (Figs. 3 and 4). For example, at Station 3 in March (Fig. 3), the variability between the four station occupations ranged from below detection limit to 1.0 μM . The dynamic changes occurred in both low flow and high flow conditions with DOP concentrations at Station 2 ranging from below detection limit to 1.2 μM in March and below detection limit to 1.4 μM in October. One possible explanation for the variability at each station is the movement of the buoyant river plume that dominates the transport of lower salinity water. The large difference in density limits the vertical mixing between the fresh warm surface plume and the colder more saline deeper water (Dagg and Breed, 2003). Wind speed and direction, tidal currents and river flow control the short-term movements of the buoyant plume (Dagg and Breed, 2003).

When samples from the river are included, there is a correlation between DOP and salinity (Fig. 5). However, no samples were collected between the zero salinity river and salinity 16. Examination of samples from the higher salinities indicates little correlation with salinity.

Indeed any given salinity may yield DOP values ranging from below detection limit (0.6 μM) to above 1.3 μM as evidenced by a sample collected at salinity 26 in October. This may be due to the fact that while salinity is an indicator of what fraction of a water mass is riverine, it gives no indication of time since discharge from the river. Despite the fact that a lack of samples at lower-salinities precludes any definitive conclusion with regard to the relationship with salinity, clearly salinity is not the master variable within the higher productivity region of the plume (Dagg and Breed, 2003).

In addition to being a source of DOP, the Mississippi River also supplies a large amount of suspended sediment (TSM) to the coastal zone (Fig. 6). However, the correlation between DOP and TSM is weaker during low flow (October) than high flow (March) conditions. This is most pronounced for the river samples where TSM decreases from 50 to 30 mg L^{-1} while the DOP remains high or even slightly increases during low flow conditions indicating sources within the river basin are different. Within the plume region, TSM is affected by dilution, settling and resuspension. DOP is also influenced by these processes but is also impacted by the biological cycle within the plume resulting in weak correlation. Therefore, for any given TSM concentration, the DOP concentration may range from below detection limit to 1.5 μM .

Since no measurements of primary productivity were made on these cruises, chlorophyll *a* measurements were used to infer biological activity. Previous work has shown correlations between primary production and high concentrations of DOP and DOC due to release of DOP by bacterial grazing (Pakulski et al., 2000). There was not a linear relationship between

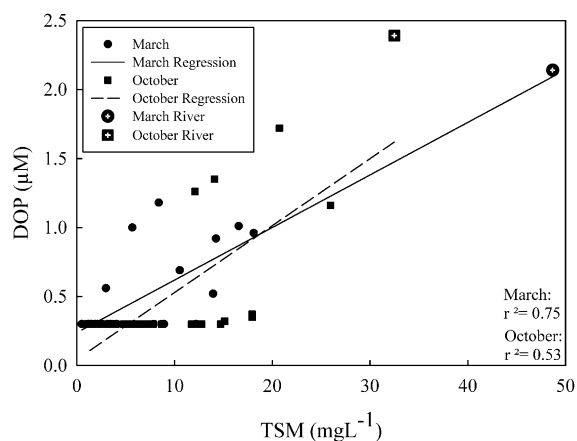


Fig. 6. DOP concentrations as a function of total suspended matter for both sampling periods. Symbols are the same as Fig. 5.

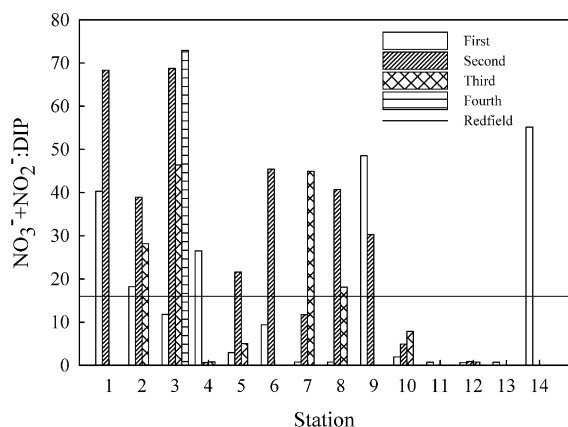


Fig. 7. $\text{NO}_3^- + \text{NO}_2^-$:DIP surface water ratios at each station in March. Each bar represents the first, second, third or fourth station occupation. The line indicates the theoretical Redfield N:P ratio of 16:1.

chlorophyll *a* and DOP in the MRP for either sampling period (data not shown). The highest DOP concentrations occurred in areas of lower chlorophyll *a* concentrations. The river stations and stations near the river mouth for both March and October had the highest DOP concentrations but some of the lower chlorophyll *a* concentrations due to light limitations on productivity in the highly turbid river. Even with these river or near river stations excluded there would still exist a poor relationship with chlorophyll *a*. In the MRP, higher primary production occurred in mid-salinity regions where there is sufficient light and nutrient supply (Gardner et al., 1996; Lohrenz et al., 1999; Pakulski et al., 2000; Dagg and Breed, 2003). However, for both March and October, the areas of highest chlorophyll *a* (Stations 2 and 3) in the mid-plume region did not have measurable ($>0.3 \mu\text{M}$) DOP. In March, the stations with higher ($1 \mu\text{M}$) DOP (Stations 1, 2 and 6) also had higher chlorophyll *a* concentrations, but not all stations with higher chlorophyll *a* had higher DOP (Stations 2, 4, 9 and 10). Previous researchers (Monaghan and Ruttenberg, 1999; Pakulski et al., 2000) have observed a correlation between chlorophyll *a* and DOP concentrations however we did not observe this on either cruise as the high chlorophyll mid plume regions always contained low ($<70.6 \mu\text{M}$) DOP concentrations.

Within the Mississippi River plume, there was no linear relationship between DOC and DOP during either sampling period (data not shown). Similar to salinity, there were a wide range of DOP concentrations for a measured DOC concentration. For instance, during the October sampling period, there were several stations which had DOC concentrations between 100 and $200 \mu\text{M}$; while most of the DOP concentrations

were below the detection limit, there were a few concentrations that ranged between 0.5 and $1.5 \mu\text{M}$. In both March and October, there was a general trend of higher DOP concentrations in the mid-salinity that was not manifested in the DOC pool. At no stations did higher DOP and DOC concentrations occur simultaneously. Since DOP is a small component of DOC it is not surprising for both to be either influenced to a differing degree by the same processes or affected by different processes in the water column.

Nitrogen to phosphorus molar ratios were calculated in order to evaluate the relationships between nitrogen and phosphorus cycling, as much more previous research has been conducted on nitrogen in the MRP (Lopez-Veneroni and Cifuentes, 1994; Turner and Rabalais, 1994; Gardner et al., 1996). For the March cruise, the $\text{NO}_3^- + \text{NO}_2^-$ /DIP ratio varied considerably with approximately half with high ratios and half with low ratios (Fig. 7). In October, the ratios were all consistently low and some stations were lower than 1 (Fig. 8). This indicates the possibility of some nitrogen stress in the system during October that only occurred at the far field stations in March. Several studies have found that there may be nitrogen limitation during periods of low river flow, when there is more seawater influence in coastal areas (Myers and Iverson, 1981; Fulmer, 1997; Mortazavi et al., 2000; Labry et al., 2002). The consistency in the $\text{NO}_3^- + \text{NO}_2^-$ /DIP ratios may indicate that inorganic nitrogen and phosphorus are closely related in the MRP for each sampling period, however ratios change with the seasons due to decreased riverine nutrient input during low winter river flows and less bacterial mineralization of refractory DON (Lopez-Veneroni and Cifuentes, 1994; Lohrenz et al., 1997). For the

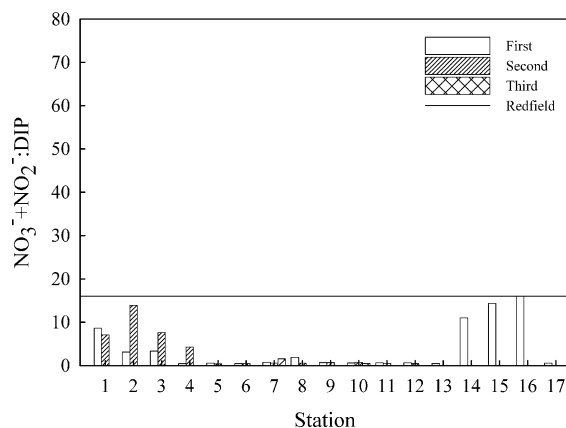


Fig. 8. $\text{NO}_3^- + \text{NO}_2^-$:DIP surface water ratios at each station in October. Each bar represents the first, second or third station occupation. The line indicates the theoretical Redfield N:P ratio of 16:1.

samples which had DOP concentrations less than the detection limit but higher than baseline (all samples were above baseline), 1/2 the detection limit was used to calculate DON/DOP ratios. In contrast to the $\text{NO}_3^- + \text{NO}_2^-/\text{DIP}$ ratios, the DON/DOP ratios showed little difference between March and October (Figs. 9 and 10). There was a large amount of variability in the ratios within each sampling period as well as between the sampling periods. The ratios range from approximately 8 to 44 in March and less than 10 to 66 in October. The variability of the ratios is an indication that DOP and DON are not affected by the same processes within the MRP as DOP has been found to be preferentially mineralized when compared to DON and DOC (Clark et al., 1998; Thomson-Bulldis and Karl, 1998; Kolowitz et al., 2001) resulting in the nitrogen enriched ratios we observed for both cruises. DOP is therefore more labile to phytoplankton than DON in these systems, leading to a shorter turnover times in coastal regions (Suzumura et al., 1998; Benitez-Nelson and Buesseler, 1999).

3.2. Colloidal DOP

The colloidal fraction of DOP was measured to gain a better understanding on the cycling of TDP in the MRP. It was initially hypothesized that freshly liberated DOP would be high molecular weight (HMW) material and DOP further from the source would be low molecular weight (LMW) due to processes such as photodegradation and bacterial utilization which have been shown to change the size spectrum of other biologically produced molecules (Cotner and Gardner, 1993; Wetzel et al., 1995; Moran and Zepp, 1997). HMW-DOP may

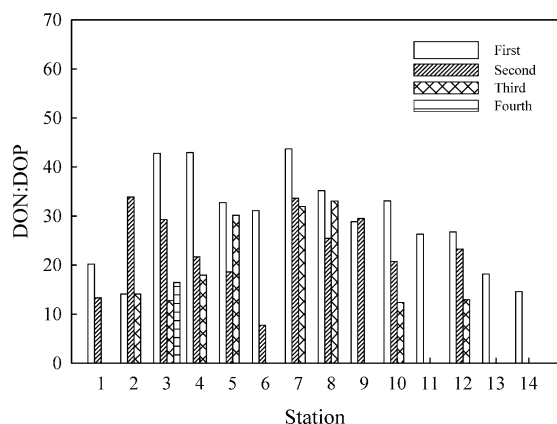


Fig. 9. DON:DOP surface water ratios at each station in March. Each bar represents the first, second, third or fourth station occupation. If DOP concentrations were below detection limit, a value of $0.3 \mu\text{M}$ was used to calculate the ratio.

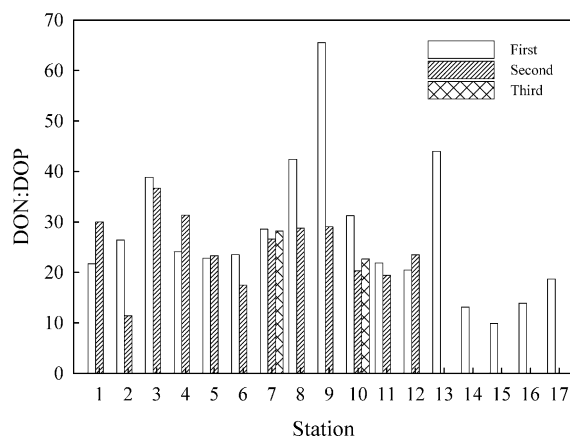


Fig. 10. DON:DOP surface water ratios at each station in October. Each bar represents the first, second or third station occupation. If DOP concentrations were below detection limit, a value of $0.3 \mu\text{M}$ was used to calculate the ratio.

consist of material from terrigenous origin (Pakulski et al., 2000) or in situ biological origin, like DNA and RNA (Minear, 1972; Suzumura et al., 1998; Kolowitz et al., 2001), while LMW-DOP is hypothesized to consist of smaller particles of biological origin (Benitez-Nelson, 2000). There was no measurable amount of colloidal DOP during either sampling period (data not shown) even in the river where HMW dissolved organic material is a major fraction in the carbon pool (Opsahl and Benner, 1998). Since we used concentration factors between 10 and 20, if colloidal DOP was only 5% of the total, it would have doubled the analytical signal for the retentate samples. This clearly did not occur, therefore we conclude that during these two sampling periods, colloidal DOP was less than 5% of the total DOP pool. This percentage is quite low when compared to previous research which has shown colloidal DOP accounting for 20–50% of the TDP (Ridal and Moore, 1990; Bauer et al., 1996; Clark et al., 1998; Suzumura et al., 1998; Clark et al., 1999; Hilger et al., 1999; Benitez-Nelson, 2000). The low HMW-DOP concentrations that were measured may be an indication that the HMW-DOP in the plume is labile and is being readily utilized which is consistent with the high bacterial productivity reported previously (Chin-Leo and Benner, 1992; Gardner et al., 1994; Benner and Opsahl, 2001).

3.3. Depth distributions

DOP concentrations were also measured at various depths at each station (data not shown). A majority of the concentrations at depth were below detection limit ($0.6 \mu\text{M}$). Concentrations were not elevated in the

bottom waters at any station, showing no evidence that resuspension or influx of open ocean waters were sources of DOP to the bottom water. Since the coastal waters are a highly stratified two layer system (buoyant river plume over high salinity cooler water), the bottom waters only act as a conduit for the transport of particulate materials out of the surface waters to the seabed and provide no forms of dissolved phosphate back to the surface waters.

4. Summary and conclusions

In summary, the abundance of DOP varies spatially in the plume, with the highest concentrations of DOP in the river and lowest further away from the river. However, there is only a slight correlation between DOP concentrations and salinity or suspended matter, especially within the higher salinities. Correlations with chlorophyll *a* and DOC are even weaker. While DIP is closely related to $\text{NO}_3^- + \text{NO}_2^-$, DOP and DON appear to cycle independently. DOP concentrations change on a time scale of less than 2–3 days as evidenced by repeat occupations of stations on each cruise. The lack of colloidal DOP in the Mississippi River plume indicates that any freshly released high molecular weight biological phosphorus must be utilized or decomposed on the time scale of the repeat occupation of stations. Only with continued field measurements or long-term monitoring and controlled experiments will the factors influencing DOP concentrations be elucidated in this study region.

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